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# Estimation of Enthalpy of Bio-oil Vapor and Heat Required for Pyrolysis of Biomass

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**ABSTRACT:** A method is proposed to estimate the enthalpy of bio-oil in vapor phase,  $H_{bo}$ , as a function of temperature in the range of 298.15–1000 K, of which experimental determination has not been done so far. The two equations proposed in this work allow estimation of the standard enthalpy of formation,  $H_{bo,0}$ , and the difference in the enthalpy between 298.15 K and a given temperature,  $\Delta H_{bo}(T)$ , respectively, only based on the overall C, H and O contents of crude bio-oil of that N and S contents are lower than 0.5 and 0.1 wt%-daf, respectively. These equations were optimized using thermodynamic data of 290 and 141 organic compounds for  $H_{bo,0}$ , and  $\Delta H_{bo}(T)$ , respectively. Given the yields of bio-oil, char and gas, the elemental compositions of the bio-oil and char, and chemical composition of the gas, the proposed equations predict the heat required for the biomass pyrolysis,  $Q_{py}(T_{py})$ , which is defined as the enthalpy difference between the products at the pyrolysis temperature,  $T_{py}$ , and biomass at 298.15 K. The predicted  $Q_{py}$  at  $T_{py} = 773\text{--}823$  K for five different types of dry biomass was in the range of 1.1–1.6 MJ kg<sup>-1</sup>.

## 1. INTRODUCTION

Estimation of the amount of heat required for the pyrolysis of biomass is an essential task in designing reactor systems for converting biomass to liquid (*i.e.*, bio-oil), biochar and/or gas. The quantity of heat of biomass pyrolysis, which is hereafter referred to as  $Q_{py}$ , is generally given by the following equation:

$$Q_{py} = H_{char}(T_{out}) + H_{bo}(T_{out}) + H_{gas}(T_{out}) - H_{biomass}(T_{in}) \quad (1)$$

where  $T_{\text{in}}$  and  $T_{\text{out}}$  are the temperature of the biomass at the inlet of pyrolyzer and that of the pyrolysis product at the outlet, respectively.  $T_{\text{out}}$  of a pyrolysis product may not necessarily be the same as that of the other products.  $H_i$  is the enthalpy of a product  $i$  or the parent biomass. It is noted that  $H_{\text{bo}}$  is the enthalpy of bio-oil in form of vapor, assuming that  $T_{\text{out}}$  is high enough to avoid the condensation of the bio-oil. The enthalpy of steam is included in  $H_{\text{gas}}(T_{\text{out}})$ .

Among the enthalpies of the pyrolysis products,  $H_{\text{gas}}$  can be estimated accurately as a function of temperature, if the yields of the individual gaseous products are known. Thermodynamic databases are available for gaseous species such as  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , lower hydrocarbons and other minor gases that contain nitrogen or sulfur. The enthalpy of each gaseous species  $j$  is given from its standard enthalpy of formation ( $H_{j,0}$ ) and heat capacity ( $C_{p,j}$ ) as

$$H_j(T) = H_{j,0} + \int_{298.15}^T C_{p,j}(T) dT \quad (2)$$

The enthalpy of char,  $H_{\text{char}}(T)$ , can be estimated in the same way as above:

$$H_{\text{char}}(T) = H_{\text{char},0} + \int_{298.15}^T C_{p,\text{char}}(T) dT \quad (3)$$

The standard enthalpy of char,  $H_{\text{char},0}$ , is directly calculated from the heat of combustion, or otherwise from the elemental composition. The heat capacity can be given as a function of temperature.<sup>1,2</sup>

Unlike in the case of solid and gaseous pyrolysis products, the determination or estimation of the enthalpy of bio-oil vapors,  $H_{bo}$ , is not an easy task. Bio-oil is generally a mixture of hundreds or thousands of compounds, and it is virtually impossible to identify all of them.<sup>3,4</sup> The overall standard enthalpy of formation of condensed bio-oil can be calculated from its heat of combustion and elemental composition, but it is impossible to measure the heat of vaporization because the vaporization and condensation of bio-oil are generally irreversible.<sup>5-7</sup> It is thus needed to develop a method to estimate  $H_{bo}$ .

There have been reports on the heats of pyrolysis of cellulose and biomass as summarized by Milosavljevic *et al.*<sup>8</sup> and Haseli *et al.*<sup>2</sup>, indicating wide range of heats of pyrolysis (from endothermic to exothermic), and often inconsistent with each other. Such variety of the reported heats of pyrolysis may be due to the range of temperatures, heating rates, and other conditions that influence the secondary reactions of the volatiles released during biomass pyrolysis.<sup>9</sup>

Differential scanning calorimetry (DSC) has been employed to determine the heat of pyrolysis.<sup>9-13</sup> DSC quantitatively measures the overall or apparent heat capacity of solid upon heating, which involves heat of reaction and also heat of vaporization of the volatile matters. Heat of reaction is normally calculated by integrating such heat capacity with respect to time, but it is different from the quantity of heat that is the focus of the present study, *i.e.*, above-defined quantity of heat,  $Q_{py}$ , which involves the enthalpy of vaporized bio-oil and gas. In DSC analyses, the enthalpy of a vaporized volatile matter, released from the pyrolyzing solid, cannot be determined. However, in practical applications it is

important to take this enthalpy into consideration regardless of the time-temperature history and extent of the secondary pyrolysis of the volatile matter.

Daugaard and Brown<sup>14</sup> measured  $Q_{py}$  for pyrolysis of several different types of biomass at 773 K in a fluidized bed pyrolyzer with a special feature that allowed them to measure the net input of heat needed to pyrolyze the biomass. They reported that the pyrolysis was endothermic with  $Q_{py}$  in a range of 0.8–1.6 MJ (kg-dry-biomass)<sup>-1</sup>. Although, the reported data give a good reference to the estimation of  $Q_{py}$  for the fluidized bed pyrolyzer at 773 K, a general method for the estimation of  $Q_{py}$  under a variety of pyrolysis conditions is needed. In particular, the estimation of enthalpy of bio-oil vapors, together with that of the gas and char, is necessary.

$$H_{bo}(T) = H_{bo,0} + \Delta H_{bo} = H_{bo,0} + \int_{298.15}^T C_{p,bo}(T) dT \quad (4)$$

where  $H_{bo,0}$  and  $C_{p,bo}$  are the standard heat of formation and heat capacity of bio-oil vapors, respectively. In the present study, a method to estimate  $H_{bo,0}$  and  $\Delta H_{bo}$  of bio-oil vapors only from its elemental composition is proposed and its accuracy is examined. In addition,  $Q_{py}$  is estimated based on Eqs.1–4 and the quantitative pyrolysis product distributions for five different biomass samples pyrolyzed in a screw-conveyer pyrolyzer.

## 2. EXPERIMENTAL

**2.1. Biomass Samples.** Five biomass samples, cedar (*cryptomeria japonica*), pine (*larix kaempferi*), willow (*salix*), bamboo (*f. pubescens*) and sasa bamboo (*sasa kurilensis*) were

used. Table 1 shows the calorific values and atomic compositions of the samples. The cedar, bamboo and sasa bamboo were in forms of rectangular chips with average sizes of *ca.* 10x10x2 mm<sup>3</sup>, *ca.* 10x4x4 mm<sup>3</sup> and *ca.* 10x4x4 mm<sup>3</sup>, respectively. The pine and willow sawdust was sieved to collect fractions retained between 1 and 5 mm sieves. The biomass samples were dried in air at 383 K for 6 h prior to use.

**2.2. Pyrolysis.** Figure 1 shows a schematic diagram of the pyrolysis apparatus used in this work. The pyrolyzer was a horizontal screw-conveyer reactor that consisted of SUS316 tube with an inner diameter of 50 mm. The biomass was fed into the pyrolyzer at a constant rate of 260–270 g·h<sup>-1</sup>, while N<sub>2</sub> was supplied from the hopper and also from the char collector at a total flow rate of 2.0 L min<sup>-1</sup> at 101 kPa and 298 K. The temperature inside the reactor was defined as that inside the hollow shaft of the screw. As seen in Figure 1, there was a temperature gradient within the zone ranging from  $L = 0$  (inlet) to  $L = 150$  mm under each condition for heating the pyrolyzer. The maximum temperature,  $T_{py}$ , at  $L = 150$  mm, was set at 773 or 823 K while 523 or 533 K at the inlet, respectively. The speed of screw rotation was adjusted so that the average residence time of the solid within the 150 mm long zone was 47 s unless otherwise noted. The average heating rate of the solid, if its temperature at a position  $L$ , was the same as that shown in Figure 1, was estimated to be 6.2 and 5.3 K·s<sup>-1</sup> at  $T_{py} = 823$  and 773 K, respectively. For the pyrolysis of the cedar with  $T_{py} = 773$  K, the average solid residence time was varied in a range from 47 to 470 s by changing the rotation speed of the screw.

The solid pyrolysis product, char, dropped into the collector where it was allowed to cool to ambient temperature. The volatiles were cooled to 423, 273, 233 and 203 K in the aerosol filter, the first, second and third condensers in series.<sup>15</sup> Quantitative condensation of water and condensable organic compounds with carbon number greater than five was confirmed in preliminary experiments. The total mass of the condensables was measured accurately by weighing the condensers before and after the run. The water contained in the condensed liquid was quantified by a Karl-Fischer titrimetry. The yield of the water-free organic condensables, which was defined as bio-oil, was determined by the difference between the yields of the condensables and water. The non-condensable gases (H<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>1</sub>–C<sub>4</sub> hydrocarbons), methanol and acetaldehyde were collected in the gasbag and quantified by gas chromatography.<sup>15</sup> The total product recovery was 99–101% on mass basis. Table 2 summarizes the molar yields of products of pyrolysis at  $T_{py} = 823$  K. The individual yields have been normalized by the total product recovery.

### **3. DEVELOPMENT OF METHOD TO ESTIMATE ENTHALPY OF CHAR, GAS AND BIO-OIL VAPOR AND HEAT REQUIRED FOR PYROLYSIS**

**3.1. Estimation of enthalpy of char, gas and bio-oil vapor and heat required for pyrolysis.** The heat required for the pyrolysis at a given peak temperature  $T_{py}$  is defined by the following equation.

$$Q_{py} = H_{char}(T_{py}) + H_{bo}(T_{py}) + H_{gas}(T_{py}) - H_{biomass,0}(T = 298.15K) \quad (5)$$



$H_{\text{char}}$ ,  $H_{\text{bo}}$  and  $H_{\text{gas}}$  are the enthalpies of char, water-free bio-oil and that of gas (*i.e.*, non-condensable gases and water vapor), and expressed by Eqs. 6, 7 and 8, respectively.

$$H_{\text{char}}(T_{\text{py}}) = H_{\text{char},0} + \Delta H_{\text{char}}(T_{\text{py}}) = H_{\text{char},0} + \bar{C}_{\text{p, char}}(T_{\text{py}} - 298.15) \quad (6)$$

$$H_{\text{bo}}(T_{\text{py}}) = H_{\text{bo},0} + \Delta H_{\text{bo}}(T_{\text{py}}) = H_{\text{bo},0} + \int_{298.15}^{T_{\text{py}}} C_{\text{p, bo}}(T) dT \quad (7)$$

$$H_{\text{gas}}(T_{\text{py}}) = H_{\text{gas},0} + \Delta H_{\text{gas}}(T_{\text{py}}) = H_{\text{gas},0} + \int_{298.15}^{T_{\text{py}}} C_{\text{p, gas}}(T) dT \quad (8)$$

Enthalpy of product  $i$  (= char, gas or bio-oil) is the sum of standard enthalpy of formation at 298.15 K ( $H_{i,0}$ ) and quantity of heat required for increasing its temperature from 298.15 K to  $T_{\text{py}}$ .

**3.2. Enthalpy of formation of char.**  $H_{\text{char},0}$  was calculated from the higher heating value of the char, HHV, which was estimated by well known Dulong's equation<sup>16</sup>,

$$\text{HHV} [\text{MJ-HHV/kg-dry}] = 33.8m_{\text{C}} + 144.2(m_{\text{H}} - m_{\text{O}} / 7.94) \quad (9)$$

where  $m_{\text{C}}$ ,  $m_{\text{H}}$  and  $m_{\text{O}}$  are the contents of carbon, hydrogen and oxygen on the basis of ash-free mass of char. Properties of the chars from the pyrolysis at  $T_{\text{py}} = 823$  K are presented in Table 3. Contribution of nitrogen and sulfur to HHV was ignored because their contents in the char were as low as 0.1–0.5 wt%-daf and below 0.1 wt%-daf, respectively.

**3.3. Enthalpy of formation of gas.**  $H_{\text{gas},0}$  was established by referring to gas phase thermodynamic data for the gaseous compounds ( $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_1\text{--C}_4$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CHO}$  and  $\text{H}_2\text{O}$ ) that are available in NIST Chemistry WebBook.<sup>17</sup>

$$H_{\text{gas},0} = \sum_{j=1}^n H_{j,0} \quad (10)$$

In the above equation,  $j$  and  $n$  indicate gaseous species and the total number of compounds involved in the gaseous products, respectively.

**3.4. Enthalpy of formation of bio-oil.**  $H_{\text{bo},0}$  was estimated by an equation that has been developed in the present study, *i.e.*,

$$\begin{aligned} \Delta H_{\text{bo},0,\text{calc}} = & a + b_1 \left( \frac{\text{H}}{\text{C}} \right) + b_2 \left( \frac{\text{H}}{\text{C}} \right)^2 + b_3 \left( \frac{\text{H}}{\text{C}} \right)^3 + b_4 \left( \frac{\text{H}}{\text{C}} \right)^4 \\ & + c_1 \left( \frac{\text{O}}{\text{C}} \right) + c_2 \left( \frac{\text{O}}{\text{C}} \right)^2 + c_3 \left( \frac{\text{O}}{\text{C}} \right)^3 + c_4 \left( \frac{\text{O}}{\text{C}} \right)^4 \end{aligned} \quad (11)$$

This equation gives  $H_{\text{bo},0}$  in a unit of  $\text{kJ mol}^{-1}$  of a water free bio-oil that has an overall H/C atomic ratio (H/C) and O/C ratio (O/C). In Eq. 11,  $a$ ,  $b_1$ – $b_4$  and  $c_1$ – $c_4$  are constants. In developing this equation, standard enthalpies of formation of 290 organic compounds (hydrocarbons and oxygen-containing compounds; *see* Table 4) were calculated by Eq. 11, and compared individually with values available in NIST Chemistry WebBook.<sup>1</sup> However, gas phase thermodynamic data of several compounds abundant in bio-oil, such as levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) and hydroxyacetone (1-hydroxy-2-propanone), were not available. The set of  $a$ ,  $b_1$ – $b_4$  and  $c_1$ – $c_4$  was optimized by a general method of least square so that the sum of squared residuals between calculated and literature values, *i.e.*,

$$\sum_{j=1}^{290} (H_{j,0,calc} - H_{j,0})^2 \quad (12)$$

was minimized. A commercially available software, Solver (within Microsoft Excel), was used for the optimization. The results of the optimization will be reported later.

**3.5. Specific heats of char, gas and bio-oil.** The specific heats,  $C_{p,i}$ 's, of the bio-oil and gas were given as a function of temperature while a constant value was assumed for that of the char. Figure 2 shows specific heat of char reported by Merrick<sup>1</sup> and that calculated by an equation employed by Haseli *et al.*<sup>2</sup> Average values for these specific heats are 0.022 and 0.019 kJ mol<sup>-1</sup>C<sup>-1</sup> over a temperature range of 300–823 K. In the present study,  $\bar{C}_{p,char}$  was therefore assumed to be 0.02 kJ mol<sup>-1</sup>C<sup>-1</sup>.  $C_{p,gas}$  was given as a function of temperature from the database.<sup>17</sup>

$\Delta H_{bo}(T_{py})$  was estimated from H/C and O/C ratios of the bio-oil. In preliminary try-and-error examination, the present authors found that enthalpies of many organic compounds in the gas phase increase with increasing temperature in trends very similar to one another. Examples are shown in Figure 3. Figure 3(a) compares  $\Delta H$  for methane with those for nine other compounds.  $\Delta H$  of a given compound  $k$  is defined by the following equation.

$$\Delta H_k(T) = \int_{298.15}^T C_{p,k}(T) dT \quad (13)$$

$\Delta H_k(T)$  of each compound as a function of temperature is available and recommended in NIST Chemistry WebBook.<sup>17</sup> Figure 3(b) illustrates the results of a trial to predict  $\Delta H$  of methane,  $\Delta H_{\text{methane}}(T)$ , from that of another compound by a simple function

$$\Delta H_{\text{methane}}(T) \approx \frac{1}{R_{\Delta H,k}} \Delta H_k(T) \quad (14)$$

where  $R_{\Delta H,k}$  is the constant for the compound  $k$ . It is seen that even such a very simple equation successfully approximates  $\Delta H_{\text{methane}}$  over the temperature range up to 1000 K. The following equation is derived from Eqs.13 and 14.

$$\Delta H_k(T) \approx R_{\Delta H,k} \Delta H_{\text{methane}}(T) = R_{\Delta H,k} \int_{298.15}^T C_{p,\text{methane}}(T) dT \quad (15)$$

Based on Eq.14, an attempt was made to estimate  $\Delta H_k(T)$  of organic compounds by deriving their  $R_{\Delta H,k}$  from H/C and O/C atomic ratios, *i.e.*, by

$$\begin{aligned} R_{\Delta H,k} &= \frac{\Delta H_k(T)}{\Delta H_{\text{methane}}(T)} \\ &= d_1 + e_1 \left( \frac{\text{H}}{\text{C}} \right) + e_2 \left( \frac{\text{H}}{\text{C}} \right)^2 + e_3 \left( \frac{\text{H}}{\text{C}} \right)^3 + e_4 \left( \frac{\text{H}}{\text{C}} \right)^4 \\ &\quad + f_1 \left( \frac{\text{O}}{\text{C}} \right) + f_2 \left( \frac{\text{O}}{\text{C}} \right)^2 + f_3 \left( \frac{\text{O}}{\text{C}} \right)^3 + f_4 \left( \frac{\text{O}}{\text{C}} \right)^4 \end{aligned} \quad (16)$$

Due to limited availability of  $C_p$  values for organic compounds compared to values for  $H_0$ , Eq.16 was applied to predict  $R_{\Delta H,k}$  for only 141 compounds (listed in Table 5). The set of parameters  $d$ ,  $e_1$ – $e_4$  and  $f_1$ – $f_4$  was optimized in the same way as that of Eq.11. The optimized Eq.16 was then applied to estimation of  $\Delta H_{\text{bo}}(T_{\text{py}})$ . The  $R_{\Delta H,\text{bo}}$  was calculated by Eq.16 from the H/C and O/C ratios of the bio-oil, which are summarized in Table 6.

## 4. RESULTS AND DISCUSSION

**4.1. Estimation of standard enthalpy of formation.** Figure 4 compares  $H_{\text{bo},0}$  calculated by Eq.11 with that available in the literature<sup>17</sup> for 290 organic compounds listed in Table 4. The optimized set of the parameters of Eq.11 are listed in Table 7. Eq.11 estimates  $H_0$  of many of 177 hydrocarbons (alkanes, alkenes, cycloalkanes, cycloalkenes and aromatics; registry numbers of 1–177) within errors within  $\pm 7 \text{ kJ mol}^{-1}$ , while underestimates  $H_0$  of pentenes ( $\text{C}_5\text{H}_{10}$ ), hexenes ( $\text{C}_6\text{H}_{12}$ ), heptenes ( $\text{C}_7\text{H}_{14}$ ) and  $\text{C}_6$ – $\text{C}_8$  cycloalkenes ( $\text{C}_6\text{H}_{10}$ ,  $\text{C}_7\text{H}_{12}$  and  $\text{C}_8\text{H}_{14}$ ) with errors of  $-7$  to  $-13 \text{ kJ mol}^{-1}$ . Estimation of  $H_0$  of specific oxygen-containing compounds (registry numbers of 178–290) causes errors greater than  $10 \text{ kJ mol}^{-1}$ . Eq.11 also overestimates  $H_0$ 's of  $\text{C}_2$ – $\text{C}_{10}$  carboxylic acids (acetic acid to decanoic acid; 212–222), an acetic acid ester (275) and alkylated benzoic acids (278, 279) with errors of  $+10$  to  $+18 \text{ kJ mol}^{-1}$ . On the other hand,  $H_0$ 's of 14 compounds (181, 224, 227, 228, 230, 231, 236, 237, 269–272, 283, 286) are underestimated with errors of 12 to  $22 \text{ kJ mol}^{-1}$ . These 14 compounds involve an aldehyde, furans, a quinone and ethers. Butanoic acid (214), ethylacetate (242) and 1,4-dioxan (272) have the same chemical formulas of  $\text{C}_4\text{H}_8\text{O}_2$ , but the errors in estimation of their  $H_0$ 's distribute over a range from  $-22$  to  $+17 \text{ kJ mol}^{-1}$ . The errors for the compounds with  $\text{C}_4\text{H}_8\text{O}$ ; 2-butanone (186), tetrahydrofuran (283) and butanal (284), distribute over another range of  $-6$  to  $+12 \text{ kJ mol}^{-1}$ . Such errors, which spread over the positive and negative values for the compounds

with the same chemical formulas, indicate a limitation of estimating  $H_0$  only from H/C and O/C ratios.

However, the extent of this limitation needs to be examined in context of the estimation  $H_0$  of real bio-oil. As shown above, Eq.11 overestimates  $\Delta H_0$ 's of carboxylic acids (212–222) with errors of 10 to 18 kJ mol-C<sup>-1</sup>. Carboxylic acids, in particular, acetic and formic are normally abundant in bio-oils, but it is safe to say that their total content in the bio-oil is well below 50%<sup>18</sup> on a carbon basis unless the pyrolysis of biomass is terminated in a very early period of bio-oil evolution for effective recovery of liquid such as wood vinegar. Dieni *et al.*<sup>19</sup> prepared a bio-oil by pyrolyzing the same cedar chips as those used in this study at 773 K with the same pyrolyzer and they found that the content of GC/MS-detectable carboxylic acid was 9% on a carbon basis. Besides this, Eq.11 also overestimates of  $H_0$ 's of acetic acid and benzoic acid esters (275, 277 and 278) with errors of 6–14 kJ mol-C<sup>-1</sup>. However, the total content of esters in bio-oil would be even less than that of carboxylic acids.<sup>18</sup> Therefore, it is safe to assume that positive errors occurring in estimating  $H_{bo,0}$  do not amount to more than a value of 10 kJ (mol-C-bio-oil)<sup>-1</sup>.

Furthermore, Eq.11 underestimates  $H_0$ 's of furan (227), its derivatives (228, 230), benzoquinone (231), dimethylether (236) and 1,4-dioxane (272) with errors of 15–22 kJ mol-C<sup>-1</sup>. Dieni *et al.*,<sup>19</sup> also reported that total content of GC/MS-detectable ketones and ethers (including cyclic ethers) in the bio-oil from the cedar was less than 20% on the carbon basis. Given the content of ketones (carbonyls), ethers and cyclic ethers in the bio-oil, underestimation of  $H_{bo,0}$ , if any, should not amount to more than 10 kJ mol-C<sup>-1</sup>.

In calculation of the heat required for pyrolysis, *i.e.*,  $Q_{py}$ , contribution of the error in estimating  $H_{bo,0}$  by Eq.11 to the total error is a function of the bio-oil yield and composition. As shown in Table 8, the error in estimation of  $H_{bo,0}$  is expected to be at most 1% of HHV of the feedstock biomass, in other words,  $0.2 \text{ MJ (kg-biomass)}^{-1}$ , assuming that Eq.11 estimates  $H_{bo,0}$  within error of  $\pm 10 \text{ kJ (mol-C-bio-oil)}^{-1}$ .

Given  $\Delta H_0$ , the standard heat of combustion,  $\Delta H_{comb}$ , of a compound can be directly calculated. Figure 5 compares heats of combustion,  $\Delta H_{comb}$  and  $\Delta H_{comb,calc}$ , which are derived from  $H_0$  and  $H_{0,calc}$ , respectively. Both  $\Delta H_{comb}$  and  $\Delta H_{comb,calc}$  are based on assumption of gas phase combustion to produce not water but steam together with  $\text{CO}_2$ . The maximum positive and negative errors are +3.5% (propanoic acid; 213) and -4.1% (2-furancarboxaldehyde; 228), respectively. For 280 compounds, among the 290 compounds listed in Table 4, the errors in estimation of  $\Delta H_{comb}$  are within  $\pm 3\%$ . Eq.11 is thus an equation that estimates heat of combustion of various types of hydrocarbons and oxygen-containing organic compounds within  $\pm 3\%$  errors despite relying only on H/C and O/C ratios as the basis for its calculation.

**4.2. Estimation of  $\Delta H$  for organic compounds and bio-oil.** The optimized set of parameters of Eq.16 is summarized in Table 9. The results of estimation of  $\Delta H$  for the 141 compounds are presented in Figure 6. For every compound, the error in the estimation, *i.e.*,  $\Delta H_{k,calc} - \Delta H_k$ , varies with temperature since  $\Delta H_k$  is a function of temperature. Though not mentioned in Section 2.7, the set of parameters of Eq.16 was optimized so that the sum of squared residuals,

$$\sum_{k=1}^{141} (\Delta H_{k,\text{calc}} - \Delta H_k)^2 \quad (17)$$

for 1000 K was minimized, because it was found in preliminary examination that the sum of squared residuals increased monotonously with temperature. It is seen in Figure 6 that the error is smaller than  $1.5 \text{ kJ mol}^{-1}\text{C}^{-1}$  over the temperature range of 600–1000 K except for nine compounds at 1000 K and a single compound at 900 K (indicated by solid keys). The nine compounds with largest errors are formaldehyde (12), ethane (16), ethylene (25), cyclopentane (79), 2,2,3,3-tetramethylbutane (121), 2,2,4,4-tetramethylpentane (123), methoxyethane (124), oxetane (134) and benzoic acid (139). Except for compounds 79 and 139, it is unlikely that these compounds would be present in any appreciable amount in bio-oil. The 141 compounds considered include acids, cyclic ethers, ketones and phenols that are usually present in bio-oil. It is thus likely that the error in the estimation of  $\Delta H_{\text{bo}}$  at 600–1000 K is well below  $1 \text{ kJ (mol-C-bio-oil)}^{-1}$ , which is an order of magnitude smaller than that of estimation of  $H_{\text{bo},0}$ .

According to the way of evaluating error in the estimation of  $H_{\text{bo},0}$  (see Table 8), contribution of the error in estimating  $\Delta H_{\text{bo}}$  to  $Q_{\text{py}}$  was evaluated. As shown in Table 10, the error of  $\Delta H_{\text{bo}}$  is expected to be smaller than  $\pm 0.1\%$  of HHV of corresponding biomass.

**4.3. Estimation of heat required for pyrolysis of biomass.** The heats required for the pyrolysis of five different biomass samples with  $T_{\text{py}} = 823 \text{ K}$  were calculated based on the data shown in Tables 1, 2, 3 and 6. The results are shown in Table 11.  $Q_{\text{py}}$  is positive for all of the biomass, indicating that their pyrolysis is endothermic, as expected. It is also noted



that  $Q_{py}$ 's for the five different biomass samples are within a relatively narrow range of 6.7–8.4 %-HHV, 31.4–37.6 kJ mol-C<sup>-1</sup> or 1.3–1.6 MJ (kg-daf-biomass)<sup>-1</sup>. Daugaard and Brown<sup>14</sup> measured the heat required for the pyrolysis of biomass fuels at 773 K during continuous operation of a specially designed pilot-scale fluidized bed pyrolyzer, and reported that the heats for two woody and two herbaceous biomass fuels were in a range from 0.8±0.2 and 1.6±0.3 MJ kg-dry<sup>-1</sup>. This range is very similar to that seen in Table 10, although  $T_{py} = 823$  K is higher than that employed by Daugaard and Brown.<sup>14</sup> As discussed previously,  $Q_{py}$  is estimated with an error due to estimation of  $H_{bo,0}$  and  $\Delta H_{bo}$ , which are ±0.17~0.19 MJ kg-daf<sup>-1</sup> and ±0.017~0.019 MJ kg-daf<sup>-1</sup>, respectively. The maximum error is thus in a range of ±0.18–0.21 MJ kg-daf<sup>-1</sup>.

**4.4. Effect of heating rate on heat required for the pyrolysis with  $T_{py} = 773$  K.** The cedar was pyrolyzed with four different heating rates while maintaining  $T_{py} = 773$  K. The product distribution and  $Q_{py}$  are summarized in Table 12. The estimated  $Q_{py}$  is in a narrow range from 1.1 to 1.2 MJ kg<sup>-1</sup>, but it seems to increase slightly with the heating rate. The effect of heating rate on the yields of some products are clear. The H<sub>2</sub>O and CO<sub>2</sub> yields decreases with increasing heating rate, suggesting suppression of cross-linking reactions to form H<sub>2</sub>O and CO<sub>2</sub>.<sup>20-22</sup> As expected from the suppressed cross-linking, the bio-oil yield and char yield largely increases and decreases with the heating rate, respectively. Such a significant change in the product distribution is, however, associated with change in  $Q_{py}$  only by about 10%.

## 5. CONCLUSIONS

This work proposes two equations, Eqs.11 and 16, for estimation of the enthalpy of bio-oil vapor,  $H_{bo}$ , as a function of temperature only based on its contents of carbon, hydrogen and oxygen. The error of estimating,  $H_{bo}$ , although it is difficult to determine exactly, is estimated well below  $\pm 0.2$  MJ (kg-dry-biomass)<sup>-1</sup>, which is mainly contributed to by the error in estimating  $H_{bo,0}$ . Based on the estimation of  $H_{bo}$ , the heat of pyrolysis  $Q_{py}$  for five different biomass at  $T_{py} = 823$  K were estimated to be 1.3–1.6 MJ (kg-dry-biomass)<sup>-1</sup>. For the pyrolysis of cedar chips at  $T_{py} = 733$  K,  $Q_{py}$  was estimated to be 1.1–1.2 MJ (kg-dry-biomass)<sup>-1</sup> and also to increase slightly with increasing heating rate.

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## NOMENCLATURE

$C_p$  specific heat

$H$  enthalpy

$\Delta H$  Difference in enthalpy of vaporous compound or product between given temperature ( $T$ ) and 298.15 K

$\Delta H_{\text{comb}}$  Heat of combustion

$R_{\Delta H}$  Ratio of  $\Delta H$  for a compound or product to that of methane

$T$  temperature

## Subscript

0 at standard temperature (= 298.15 K)

bo bio-oil

calc calculated

CH<sub>4</sub> methane

*i* a compound or product

in inlet of pyrolyzer

*j* a compound or product

*k* a compound or product

out outlet of pyrolyzer

py pyrolysis

## TABLE Captions

**Table 1.** Properties of biomass samples.

**Table 2.** Product yields from pyrolysis of biomass with  $T_{\text{py}} = 823$  K.

**Table 3.** Properties of chars from pyrolysis at  $T_{\text{py}} = 823$  K.

**Table 4.** List of compounds with known heat of formation for vapor.

**Table 5.** List of compounds with known  $\Delta H$  as a function of temperature.

**Table 6.** H/C and O/C atomic ratios,  $H_{\text{bo},0}$  and  $R_{\Delta H,\text{bo}}$  of the bio-oils from the pyrolysis with  $T_{\text{py}} = 823$  K.

**Table 7.** Optimized parameters for Eq.11.

**Table 8.** Error in estimating  $H_{\text{bo},0}$  for the pyrolysis of biomass.

**Table 9.** Optimized parameters for Eq.16.

**Table 10.** Error in estimating  $\Delta H_{\text{bo}}$  for the pyrolysis of biomass.

**Table 11.** Heat required for the pyrolysis ( $Q_{\text{py}}$ ) with  $T_{\text{py}} = 823$  K.

**Table 12.** Effects of heating rate on the product distribution and  $Q_{\text{py}}$  for the pyrolysis of

cedar with  $T_{\text{py}} = 773 \text{ K}$ .

## FIGURE Captions

**Figure 1.** Schematic of apparatus for pyrolysis and temperature distribution in pyrolyzer.

**Figure 2.** Specific heat of char reported previously.<sup>1,2</sup>

**Figure 3.** (a) Change of enthalpy ( $\Delta H$ ) for methane and other selected compounds as a function of temperature. (b) Estimation of  $\Delta H$  of methane ( $\Delta H_{\text{methane}}$ ) from  $\Delta H$  of another compound by Eq.14 with optimized set of parameters (see Table 5).

**Figure 4.** Difference between  $H_0$  calculated by Eq.11 and that available in literature for 290 organic compounds.

**Figure 5.** Relationship between  $\Delta H_{\text{comb,calc}}$  and  $\Delta H_{\text{comb}}$  for 290 compounds.

**Figure 6.** Error in estimation of  $\Delta H$  for 141 compounds listed in Table 4. Keys:  $|\Delta H_{\text{calc}} - \Delta H| > 1.5 \text{ kJ mol}^{-1}$ .



**Table 1.** Properties of biomass samples.

Biomass	Cedar	Pine	Willow	Bamboo	Sasa bamboo
H/C atomic ratio, -	1.44	1.37	1.33	1.48	1.39
O/C atomic ratio, -	0.63	0.61	0.60	0.67	0.67
Heating value, MJ-HHV (kg-daf) <sup>-1</sup>	20.0	19.8	19.8	18.9	18.5
Heating value, kJ-HHV (mol-C) <sup>-1</sup>	472	460	456	459	448
Standard enthalpy of formation ( $H_{bm}$ ), kJ mol-C <sup>-1</sup>	-132	-130	-128	-147	-144

Remark: N and S contents were 0.2 - 0.4 wt%-daf and less than 0.02 wt%-daf, respectively.

**Table 2.** Product yields from pyrolysis of biomass with  $T_{py} = 823$  K.

Biomass	Cedar	Pine	Willow	Bamboo	Sasa bamboo
Product	Yield on carbon basis, mol-C (100-mol-C-biomass) <sup>-1</sup>				
Char	35.7	35.6	34.1	40.1	33.2
Gas					
CO	9.68	11.59	9.57	7.64	10.088
CO <sub>2</sub>	5.75	6.38	7.24	6.77	6.752
CH <sub>4</sub>	2.90	3.43	2.55	2.29	2.684
C <sub>2</sub> H <sub>4</sub>	0.89	1.01	1.16	0.75	0.969
C <sub>2</sub> H <sub>6</sub>	0.52	0.63	0.58	0.51	0.495
C <sub>3</sub> H <sub>6</sub>	0.68	0.90	0.88	0.49	0.674
C <sub>3</sub> H <sub>8</sub>	0.15	0.17	0.14	0.12	0.107
C <sub>4</sub> H <sub>8</sub>	0.38	0.45	0.54	0.33	0.340
CH <sub>3</sub> CHO	0.03	0.47	0.22	0.109	0.295
CH <sub>3</sub> OH	0.22	0.04	0.04	0.09	0.105
Tar	43.1	39.3	43.0	40.8	44.3
	Yield, mol-compound (100-mol-C-biomass) <sup>-1</sup>				
H <sub>2</sub> O	23.5	24.1	26.8	24.2	25.8
H <sub>2</sub>	0.6	1.7	1.8	0.4	0.8

**Table 3.** Properties of chars from pyrolysis at  $T_{\text{py}} = 823$  K.

Parent biomass of char	Cedar	Pine	Willow	Bamboo	Sasa bamboo
H/C ratio, -	0.57	0.52	0.47	0.50	0.52
O/C ratio, -	0.12	0.073	0.14	0.089	0.14
Heating value, MJ-HHV (kg-daf) <sup>-1</sup>	31.6	33.9	29.8	32.5	30.6
Heating value, kJ-HHV mol-C <sup>-1</sup>	459	464	441	456	450
Standard enthalpy of formation $H_{0,\text{char}}$ , kJ mol-C <sup>-1</sup>	-16	-3.6	-20	-8.8	-18
Remark: N and S contents in the chars were 0.1 - 0.5 wt%-daf and less than 0.1 wt%-daf, respectively.					

**Table 4.** List of compounds with known heat of formation for vapor.

number	name	formula	$\Delta H_{0,\text{gas}}$ kJ mol <sup>-1</sup> C <sup>-1</sup>
1	Pentane	C <sub>5</sub> H <sub>12</sub>	-146.8
2	Hexane	C <sub>6</sub> H <sub>14</sub>	-167.1
3	Heptane	C <sub>7</sub> H <sub>16</sub>	-187.8
4	Hexane, 2-methyl-	C <sub>7</sub> H <sub>16</sub>	-195.0
5	Pentane, 2,4-dimethyl-	C <sub>7</sub> H <sub>16</sub>	-202.1
6	Pentane, 2,2-dimethyl-	C <sub>7</sub> H <sub>16</sub>	-206.2
7	Pentane, 3,3-dimethyl-	C <sub>7</sub> H <sub>16</sub>	-201.5
8	Butane, 2,2,3-trimethyl-	C <sub>7</sub> H <sub>16</sub>	-204.8
9	Pentane, 3-ethyl-	C <sub>7</sub> H <sub>16</sub>	-189.7
10	Pentane, 2,3-dimethyl-	C <sub>7</sub> H <sub>16</sub>	-199.2
11	Hexane, 3-methyl-	C <sub>7</sub> H <sub>16</sub>	-192.3
12	Octane	C <sub>8</sub> H <sub>18</sub>	-208.7
13	Pentane, 2,2,4-trimethyl-	C <sub>8</sub> H <sub>18</sub>	-224.1
14	Heptane, 2-methyl-	C <sub>8</sub> H <sub>18</sub>	-215.5
15	Heptane, 3-methyl-	C <sub>8</sub> H <sub>18</sub>	-212.6
16	Pentane, 2,3,4-trimethyl-	C <sub>8</sub> H <sub>18</sub>	-217.4
17	Hexane, 2,3-dimethyl-	C <sub>8</sub> H <sub>18</sub>	-213.9
18	Hexane, 3,4-dimethyl-	C <sub>8</sub> H <sub>18</sub>	-213.0
19	Pentane, 3-ethyl-2-methyl-	C <sub>8</sub> H <sub>18</sub>	-211.2
20	Hexane, 3-ethyl-	C <sub>8</sub> H <sub>18</sub>	-210.9
21	Butane, 2,2,3,3-tetramethyl-	C <sub>8</sub> H <sub>18</sub>	-226.2
22	Pentane, 3-ethyl-3-methyl-	C <sub>8</sub> H <sub>18</sub>	-215.0
23	Hexane, 2,5-dimethyl-	C <sub>8</sub> H <sub>18</sub>	-222.6
24	Heptane, 4-methyl-	C <sub>8</sub> H <sub>18</sub>	-212.1
25	Hexane, 2,4-dimethyl-	C <sub>8</sub> H <sub>18</sub>	-219.4
26	Hexane, 2,2-dimethyl-	C <sub>8</sub> H <sub>18</sub>	-224.7
27	Hexane, 3,3-dimethyl-	C <sub>8</sub> H <sub>18</sub>	-220.1
28	Pentane, 2,2,3-trimethyl-	C <sub>8</sub> H <sub>18</sub>	-220.1
29	Pentane, 2,3,3-trimethyl-	C <sub>8</sub> H <sub>18</sub>	-216.4
30	Nonane	C <sub>9</sub> H <sub>20</sub>	-228.3
31	Pentane, 2,2,4,4-tetramethyl-	C <sub>9</sub> H <sub>20</sub>	-241.5
32	Hexane, 2,2,5-trimethyl-	C <sub>9</sub> H <sub>20</sub>	-253.1
33	Heptane, 2,2-dimethyl-	C <sub>9</sub> H <sub>20</sub>	-246.1
34	Hexane, 2,3,5-trimethyl-	C <sub>9</sub> H <sub>20</sub>	-242.6
35	Pentane, 3-ethyl-2,4-dimethyl-	C <sub>9</sub> H <sub>20</sub>	-227.4
36	Decane	C <sub>10</sub> H <sub>22</sub>	-249.7
37	Nonane, 5-methyl-	C <sub>10</sub> H <sub>22</sub>	-258.6
38	Hexane, 2,2,5,5-tetramethyl-	C <sub>10</sub> H <sub>22</sub>	-285.0
39	Nonane, 2-methyl-	C <sub>10</sub> H <sub>22</sub>	-260.2
40	Undecane	C <sub>11</sub> H <sub>24</sub>	-270.3
41	n-Dodecane	C <sub>12</sub> H <sub>26</sub>	-290.9

42	Tridecane	$C_{13}H_{28}$	-311.5
43	Tri-t-butylmethane	$C_{13}H_{28}$	-235.2
44	Tetradecane	$C_{14}H_{30}$	-332.1
45	2,2,3,3,4,4,5,5-Octamethylhexane	$C_{14}H_{30}$	-248.3
46	Hexane, 3,3,4,4-tetraethyl-	$C_{14}H_{30}$	-265.5
47	Pentadecane	$C_{15}H_{32}$	-354.8
48	Hexadecane	$C_{16}H_{34}$	-374.9
49	Heptadecane	$C_{17}H_{36}$	-393.9
50	Octadecane	$C_{18}H_{38}$	-414.6
51	Nonadecane	$C_{19}H_{40}$	-435.1
52	Eicosane	$C_{20}H_{42}$	-455.8
53	11-n-Butyldocosane	$C_{26}H_{54}$	-593.3
54	Docosane, 5-butyl-	$C_{26}H_{54}$	-587.4
55	Heneicosane, 11-decyl-	$C_{31}H_{64}$	-700.0
56	Dotriacontane	$C_{32}H_{66}$	-696.6
57	1-Pentene	$C_5H_{10}$	-22.0
58	2-Pentene, (E)-	$C_5H_{10}$	-32.0
59	2-Pentene, (Z)-	$C_5H_{10}$	-28.0
60	Cyclopentane, methyl-	$C_6H_{12}$	-106.0
61	2-Butene, 2,3-dimethyl-	$C_6H_{12}$	-70.3
62	Cyclobutane, ethyl-	$C_6H_{12}$	-27.7
63	1-Hexene	$C_6H_{12}$	-42.0
64	3-Hexene, (E)-	$C_6H_{12}$	-49.3
65	1-Pentene, 4-methyl-	$C_6H_{12}$	-49.4
66	3-Hexene, (Z)-	$C_6H_{12}$	-45.9
67	2-Hexene, (E)-	$C_6H_{12}$	-51.0
68	2-Hexene, (Z)-	$C_6H_{12}$	-47.0
69	2-Pentene, 3-methyl-, (E)-	$C_6H_{12}$	-63.5
70	2-Pentene, 3-methyl-, (Z)-	$C_6H_{12}$	-61.9
71	1-Butene, 2,3-dimethyl-	$C_6H_{12}$	-65.9
72	Pentane, 3-methylene-	$C_6H_{12}$	-56.1
73	Cyclopentane, 1,3-dimethyl-, cis-	$C_7H_{14}$	-133.6
74	Cyclopentane, 1,2-dimethyl-, cis-	$C_7H_{14}$	-129.5
75	Cyclopentane, 1,1-dimethyl-	$C_7H_{14}$	-138.3
76	Cyclopentane, 1,3-dimethyl-, trans-	$C_7H_{14}$	-135.9
77	Cyclopentane, 1,2-dimethyl-, trans-	$C_7H_{14}$	-136.7
78	1-Heptene	$C_7H_{14}$	-63.0
79	2-Heptene, (E)-	$C_7H_{14}$	-74.2
80	3-Heptene, (E)-	$C_7H_{14}$	-73.2
81	2-Heptene, (Z)-	$C_7H_{14}$	-70.7
82	3-Heptene, (Z)-	$C_7H_{14}$	-69.4
83	1,2-Diethyl-cyclopropane, trans-	$C_7H_{14}$	-49.1
84	cis-1,2-Diethylcyclopropane	$C_7H_{14}$	-44.6
85	1-Octene	$C_8H_{16}$	-82.9
86	Cyclopentane, propyl-	$C_8H_{16}$	-147.6
87	3-Hexene, 2,2-dimethyl-, (Z)-	$C_8H_{16}$	-96.6
88	3-Hexene, 2,5-dimethyl-, (E)-	$C_8H_{16}$	-119.5
89	3-Hexene, 2,2-dimethyl-, (E)-	$C_8H_{16}$	-118.0
90	2,5-Dimethyl-3-hexene, (Z)-	$C_8H_{16}$	-111.3
91	Cyclohexane, propyl-	$C_9H_{18}$	-192.4
92	Cyclopentane, butyl-	$C_9H_{18}$	-168.3

93	Cyclohexane, 1,3,5-trimethyl-, (1 $\alpha$ ,3 $\alpha$ ,5 $\alpha$ )-cis	C <sub>9</sub> H <sub>18</sub>	-215.4
94	Cyclohexane, 1,3,5-trimethyl-, (1 $\alpha$ ,3 $\alpha$ ,5 $\beta$ )-trans	C <sub>9</sub> H <sub>18</sub>	-206.6
95	1-Decene	C <sub>10</sub> H <sub>20</sub>	-124.6
96	Cyclohexane, butyl-	C <sub>10</sub> H <sub>20</sub>	-213.2
97	Cyclopentane, pentyl-	C <sub>10</sub> H <sub>20</sub>	-188.9
98	(E)-2,2,5,5-Tetramethyl-3-hexene	C <sub>10</sub> H <sub>20</sub>	-167.0
99	3-Hexene, 2,2,5,5-tetramethyl-, (Z)-	C <sub>10</sub> H <sub>20</sub>	-127.0
100	1,1,4-Trimethylcycloheptane	C <sub>10</sub> H <sub>20</sub>	-210.3
101	Cyclohexane, pentyl-	C <sub>11</sub> H <sub>22</sub>	-233.8
102	Cyclopentane, hexyl-	C <sub>11</sub> H <sub>22</sub>	-209.5
103	1-Dodecene	C <sub>12</sub> H <sub>24</sub>	-165.4
104	Cyclohexane, hexyl-	C <sub>12</sub> H <sub>24</sub>	-254.4
105	n-Heptylcyclopentane	C <sub>12</sub> H <sub>24</sub>	-230.1
106	2,3-Di-tert-butyl-2-butene, (E)-	C <sub>12</sub> H <sub>24</sub>	-149.5
107	2,3-Di-tert-butyl-2-butene, (Z)-	C <sub>12</sub> H <sub>24</sub>	-123.1
108	Heptylcyclohexane	C <sub>13</sub> H <sub>26</sub>	-275.0
109	n-Octylcyclopentane	C <sub>13</sub> H <sub>26</sub>	-250.7
110	Cyclohexane, octyl-	C <sub>14</sub> H <sub>28</sub>	-295.6
111	Cyclotetradecane	C <sub>14</sub> H <sub>28</sub>	-239.2
112	n-Nonylcyclopentane	C <sub>14</sub> H <sub>28</sub>	-271.3
113	3,4-Di-tert-butyl-3-hexene, (E)-	C <sub>14</sub> H <sub>28</sub>	-168.3
114	n-Nonylcyclohexane	C <sub>15</sub> H <sub>30</sub>	-316.2
115	1-Hexadecene	C <sub>16</sub> H <sub>32</sub>	-248.4
116	Cyclohexane, decyl-	C <sub>16</sub> H <sub>32</sub>	-336.9
117	n-Undecylcyclopentane	C <sub>16</sub> H <sub>32</sub>	-312.5
118	Cyclohexane, undecyl-	C <sub>17</sub> H <sub>34</sub>	-357.0
119	n-Dodecylcyclopentane	C <sub>17</sub> H <sub>34</sub>	-333.2
120	Dodecylcyclohexane	C <sub>18</sub> H <sub>36</sub>	-378.1
121	n-Tridecylcyclopentane	C <sub>18</sub> H <sub>36</sub>	-353.8
122	n-Tetradecylcyclopentane	C <sub>19</sub> H <sub>38</sub>	-374.4
123	n-Tridecylcyclohexane	C <sub>19</sub> H <sub>38</sub>	-398.7
124	Cyclohexane, tetradecyl-	C <sub>20</sub> H <sub>40</sub>	-419.3
125	n-Hexadecylcyclopentane	C <sub>21</sub> H <sub>42</sub>	-415.6
126	n-Pentadecylcyclohexane	C <sub>21</sub> H <sub>42</sub>	-439.9
127	n-Hexadecylcyclohexane	C <sub>22</sub> H <sub>44</sub>	-460.5
128	Cyclohexene	C <sub>6</sub> H <sub>10</sub>	-4.3
129	Cyclopentane, methylene-	C <sub>6</sub> H <sub>10</sub>	10.2
130	Cyclopentene, 1-methyl-	C <sub>6</sub> H <sub>10</sub>	-4.4
131	Cyclopentene, 3-methyl-	C <sub>6</sub> H <sub>10</sub>	9.7
132	Cyclohexene, 1-methyl-	C <sub>7</sub> H <sub>12</sub>	-81.3
133	Cyclopentene, 1-ethyl-	C <sub>7</sub> H <sub>12</sub>	-25.0
134	Cyclopentene, 3-ethyl-	C <sub>7</sub> H <sub>12</sub>	-12.4
135	Bicyclo[4.1.0]heptane	C <sub>7</sub> H <sub>12</sub>	2.0
136	Ethylidenecyclopentane	C <sub>7</sub> H <sub>12</sub>	-20.0
137	Cyclopentene, 1,2-dimethyl-	C <sub>7</sub> H <sub>12</sub>	-41.4
138	Cyclohexene, 1-ethyl-	C <sub>8</sub> H <sub>14</sub>	-63.6
139	2,4-Hexadiene, 2,5-dimethyl-	C <sub>8</sub> H <sub>14</sub>	-19.2
140	Pentalene, octahydro-, cis-	C <sub>8</sub> H <sub>14</sub>	-93.0
141	Bicyclo[3.3.0]octane, trans-	C <sub>8</sub> H <sub>14</sub>	-67.0

142	cis-Cyclooctene	C <sub>8</sub> H <sub>14</sub>	-22.7
143	Bicyclo[5.1.0]octane	C <sub>8</sub> H <sub>14</sub>	-17.0
144	Bicyclo[5.1.0]octane, cis-	C <sub>8</sub> H <sub>14</sub>	-6.1
145	Cyclooctene, trans-	C <sub>8</sub> H <sub>14</sub>	20.0
146	Bicyclo[4.2.0]octane	C <sub>8</sub> H <sub>14</sub>	-26.0
147	1-Methylbicyclo[4.1.0]-heptane	C <sub>8</sub> H <sub>14</sub>	-20.8
148	2,4-Hexadiene, 3,4-dimethyl-, (E,Z)-	C <sub>8</sub> H <sub>14</sub>	3.1
149	2,4-Hexadiene, 3,4-dimethyl-, (Z,Z)-	C <sub>8</sub> H <sub>14</sub>	-3.8
150	2,4-Hexadiene, 3,4-dimethyl-, (E,E)-	C <sub>8</sub> H <sub>14</sub>	-2.3
151	Cyclohexene, 1-methyl-4-(1-methylethyl)-	C <sub>10</sub> H <sub>18</sub>	-110.8
152	Cyclohexene, 4-methyl-1-(1-methylethyl)-	C <sub>10</sub> H <sub>18</sub>	-111.2
153	Spiro(4-5)decane	C <sub>10</sub> H <sub>18</sub>	-145.1
154	Bicyclo[3.3.2]decane	C <sub>10</sub> H <sub>18</sub>	-106.0
155	Bicyclo[5.3.0]decane	C <sub>10</sub> H <sub>18</sub>	-130.1
156	Spiro[5.5]undecane	C <sub>11</sub> H <sub>20</sub>	-188.3
157	Bicyclo[3.3.3]undecane	C <sub>11</sub> H <sub>20</sub>	-89.0
158	Meso-3,4-dicyclohexyl-2,5-dimethylhexane	C <sub>20</sub> H <sub>38</sub>	-300.0
159	Benzene	C <sub>6</sub> H <sub>6</sub>	82.9
160	Naphthalene	C <sub>10</sub> H <sub>8</sub>	150.0
161	Anthracene	C <sub>14</sub> H <sub>10</sub>	223.0
162	Phenanthrene	C <sub>14</sub> H <sub>10</sub>	202.2
163	Pyrene	C <sub>16</sub> H <sub>10</sub>	225.5
164	Styrene	C <sub>8</sub> H <sub>8</sub>	146.9
165	$\alpha$ -Methylstyrene	C <sub>9</sub> H <sub>10</sub>	118.3
166	Toluene	C <sub>7</sub> H <sub>8</sub>	50.1
167	Benzene, 1,2-dimethyl-	C <sub>8</sub> H <sub>10</sub>	19.0
168	Benzene, 1,3-dimethyl-	C <sub>8</sub> H <sub>10</sub>	17.2
169	p-Xylene	C <sub>8</sub> H <sub>10</sub>	17.9
170	Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	29.8
171	Benzene, 1,2,4-trimethyl-	C <sub>9</sub> H <sub>12</sub>	-13.9
172	Benzene, 1,2,3-trimethyl-	C <sub>9</sub> H <sub>12</sub>	-9.6
173	Benzene, 1,2,4,5-tetramethyl-	C <sub>10</sub> H <sub>14</sub>	-47.1
174	Benzene, 1,2,3,5-tetramethyl-	C <sub>10</sub> H <sub>14</sub>	-43.2
175	Benzene, 1,2,3,4-tetramethyl-	C <sub>10</sub> H <sub>14</sub>	-36.0
176	Benzene, pentamethyl-	C <sub>11</sub> H <sub>16</sub>	-67.2
177	Benzene, hexamethyl-	C <sub>12</sub> H <sub>18</sub>	-77.4
178	Methanol	CH <sub>4</sub> O	-205.0
179	Ethanol	C <sub>2</sub> H <sub>6</sub> O	-234.0
180	1,2-Ethanediol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	-394.4
181	Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	-172.0
182	Propanal	C <sub>3</sub> H <sub>6</sub> O	-188.7
183	Acetone	C <sub>3</sub> H <sub>6</sub> O	-218.5
184	1-Propanol	C <sub>3</sub> H <sub>8</sub> O	-256.0
185	Isopropyl alcohol	C <sub>3</sub> H <sub>8</sub> O	-272.8
186	2-Butanone	C <sub>4</sub> H <sub>8</sub> O	-238.6
187	1-Butanol	C <sub>4</sub> H <sub>10</sub> O	-277.0
188	2-Butanol	C <sub>4</sub> H <sub>10</sub> O	-293.1
189	Ethanol, 1,1-dimethyl-	C <sub>4</sub> H <sub>10</sub> O	-312.6
190	Cyclopentanol	C <sub>5</sub> H <sub>10</sub> O	-243.0
191	Cyclohexanol	C <sub>6</sub> H <sub>12</sub> O	-290.0
192	Cyclohexanone	C <sub>6</sub> H <sub>10</sub> O	-231.1
193	Phenol	C <sub>6</sub> H <sub>6</sub> O	-96.4

194	Benzyl alcohol	$C_7H_8O$	-94.6
195	Cycloheptanone	$C_7H_{12}O$	-248.0
196	Benzaldehyde	$C_7H_6O$	-36.8
197	Phenol, 4-methyl-	$C_7H_8O$	-125.3
198	Phenol, 3-methyl-	$C_7H_8O$	-133.6
199	Phenol, 2-methyl-	$C_7H_8O$	-128.3
200	Phenol, 2,6-dimethyl-	$C_8H_{10}O$	-157.5
201	Phenol, 4-ethyl-	$C_8H_{10}O$	-144.3
202	3-Ethylphenol	$C_8H_{10}O$	-146.2
203	Phenol, 2-ethyl-	$C_8H_{10}O$	-145.2
204	Phenol, 2-methoxy-4-methyl-	$C_8H_{10}O_2$	-291.9
205	Phenol, 2,4,6-trimethyl-	$C_9H_{12}O$	-176.9
206	Phenol, 2,4-dimethyl-	$C_8H_{10}O$	-163.0
207	Phenol, 2,5-dimethyl-	$C_8H_{10}O$	-161.7
208	Phenol, 2,3-dimethyl-	$C_8H_{10}O$	-157.3
209	Phenol, 3,5-dimethyl-	$C_8H_{10}O$	-161.6
210	Phenol, 3,4-dimethyl-	$C_8H_{10}O$	-156.6
211	Formic acid	$CH_2O_2$	-378.6
212	Acetic acid	$C_2H_4O_2$	-433.0
213	Propanoic acid	$C_3H_6O_2$	-455.0
214	Butanoic acid	$C_4H_8O_2$	-475.9
215	Pentanoic acid	$C_5H_{10}O_2$	-491.0
216	Butanoic acid, 3-methyl-	$C_5H_{10}O_2$	-502.5
217	Butanoic acid, 2-methyl-	$C_5H_{10}O_2$	-495.4
218	Hexanoic acid	$C_6H_{12}O_2$	-512.0
219	Heptanoic acid	$C_7H_{14}O_2$	-536.5
220	Octanoic acid	$C_8H_{16}O_2$	-554.5
221	Nonanoic acid	$C_9H_{18}O_2$	-575.6
222	Decanoic acid	$C_{10}H_{20}O_2$	-624.2
223	Acetic acid, phenyl ester	$C_8H_8O_2$	-279.7
224	Formic acid, ethyl ester	$C_3H_6O_2$	-361.7
225	1-Naphthalenol	$C_{10}H_8O$	-30.8
226	2-Naphthalenol	$C_{10}H_8O$	-29.9
227	Furan	$C_4H_4O$	-34.7
228	2-Furancarboxaldehyde	$C_5H_4O_2$	-149.6
229	Methyl 2-furoate	$C_6H_6O_3$	-405.0
230	2-Furanmethanol	$C_5H_6O_2$	-212.0
231	p-Benzoquinone	$C_6H_4O_2$	-120.0
232	9,10-Anthraquinone	$C_{14}H_8O_2$	-75.7
233	1,4-Naphthalenedione	$C_{10}H_6O_2$	-97.5
234	9,10-Phenanthroquinone	$C_{14}H_8O_2$	-46.6
235	Hydroquinone	$C_6H_6O_2$	-277.0
236	Dimethyl ether	$C_2H_6O$	-184.1
237	Ethane, methoxy-	$C_3H_8O$	-216.4
238	Ethoxy ethane	$C_4H_{10}O$	-252.7
239	Diisopropyl ether	$C_6H_{14}O$	-318.0
240	Di-n-propyl ether	$C_6H_{14}O$	-293.0
241	Propane, 2-ethoxy-2-methyl-	$C_6H_{14}O$	-317.8
242	Ethyl acetate	$C_4H_8O_2$	-445.4
243	Methyl propyl ether	$C_4H_{10}O$	-238.0
244	Propane, 2-methoxy-	$C_4H_{10}O$	-252.0
245	Propane, 2-methoxy-2-methyl-	$C_5H_{12}O$	-285.0

246	Butane, 1-methoxy-	C <sub>5</sub> H <sub>12</sub> O	-258.1
247	Propane, 1-ethoxy-	C <sub>5</sub> H <sub>12</sub> O	-272.2
248	Butane, 2-methoxy-2-methyl-	C <sub>6</sub> H <sub>14</sub> O	-306.5
249	Propane, 2-methyl-2-(1-methylethoxy)-	C <sub>7</sub> H <sub>16</sub> O	-358.0
250	n-Butyl ether	C <sub>8</sub> H <sub>18</sub> O	-334.0
251	Di-t-butyl ether	C <sub>8</sub> H <sub>18</sub> O	-361.1
252	Propane, 1-(1,1-dimethylethoxy)-2-methyl-	C <sub>8</sub> H <sub>18</sub> O	-368.2
253	Di-sec-butyl ether	C <sub>8</sub> H <sub>18</sub> O	-361.0
254	1-t-butoxybutane	C <sub>8</sub> H <sub>18</sub> O	-361.0
255	Butane, 2-(1,1-dimethylethoxy)-	C <sub>8</sub> H <sub>18</sub> O	-380.0
256	Butyl 1,1-dimethylpropyl ether	C <sub>9</sub> H <sub>20</sub> O	-382.2
257	Amyl-t-butyl ether	C <sub>9</sub> H <sub>20</sub> O	-380.6
258	Pentane, 1,1'-oxybis-	C <sub>10</sub> H <sub>22</sub> O	-390.0
259	Benzene, methoxy-	C <sub>7</sub> H <sub>8</sub> O	-67.9
260	Benzene, ethoxy-	C <sub>8</sub> H <sub>10</sub> O	-101.6
261	carbonic acid, diethyl ester	C <sub>5</sub> H <sub>10</sub> O <sub>3</sub>	-637.9
262	Dibenzo-p-dioxin	C <sub>12</sub> H <sub>8</sub> O <sub>2</sub>	-59.2
263	1,2-Benzenediol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	-274.8
264	Resorcinol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	-284.7
265	1,2,3-Benzenetriol	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	-434.2
266	1,3,5-Benzenetriol	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	-452.9
267	1,2,4-Benzenetriol	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	-444.0
268	Monomethyl carbonate	C <sub>2</sub> H <sub>4</sub> O <sub>3</sub>	-607.0
269	1-Propenol, (E)-	C <sub>3</sub> H <sub>6</sub> O	-169.0
270	1-Propenol, (Z)-	C <sub>3</sub> H <sub>6</sub> O	-174.0
271	Propen-2-ol	C <sub>3</sub> H <sub>6</sub> O	-176.0
272	1,4-dioxan	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	-318.0
273	2-Furanmethanol, tetrahydro-	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	-369.0
274	Propanoic acid, ethyl ester	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	-466.0
275	Acetic acid, 1-methylethyl ester	C <sub>5</sub> H <sub>10</sub> O <sub>2</sub>	-489.0
276	Benzoic acid, methyl ester	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	-269.3
277	Acetic acid, phenyl ester	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	-279.7
278	Benzoic acid, 2-methyl-	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	-320.6
279	Benzoic acid, 4-methyl-	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	-324.5
280	Benzophenone	C <sub>8</sub> H <sub>8</sub> O	-87.7
281	Benzofuran, 2,3-dihydro-	C <sub>8</sub> H <sub>8</sub> O	-46.5
282	Benzofuran	C <sub>8</sub> H <sub>6</sub> O	13.6
283	Tetrahydrofuran	C <sub>4</sub> H <sub>8</sub> O	-184.2
284	Butanal	C <sub>4</sub> H <sub>8</sub> O	-211.8
285	Prop-1-en-1,2-dimethyl-1-ol	C <sub>5</sub> H <sub>10</sub> O	-241.0
286	1-(vinylloxy)propane	C <sub>5</sub> H <sub>10</sub> O	-162.0
287	Acetylacetone	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	-376.1
288	2(3H)-Furanone, dihydro-5-methyl-	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	-406.5
289	2-Butenoic acid, methyl ester, (E)-	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	-342.0
290	2-Ethylpropenoic acid	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	-393.3



**Table 5.** List of compounds with known  $\Delta H$  as a function of temperature.

number	name	formula	$R_{\Delta H}$
-	methane	CH <sub>4</sub>	
1	methanol	CH <sub>4</sub> O	1.263
2	ethanol	C <sub>2</sub> H <sub>6</sub> O	1.009
3	1-Propanol	C <sub>3</sub> H <sub>8</sub> O	0.927
4	2-Prpanol	C <sub>3</sub> H <sub>8</sub> O	0.927
5	1,2-Ethenediol	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	1.151
6	1-Butanol	C <sub>4</sub> H <sub>10</sub> O	0.882
7	2-Butanol	C <sub>4</sub> H <sub>10</sub> O	0.882
8	Ethanol, 1,1-dimethyl-	C <sub>4</sub> H <sub>10</sub> O	0.882
9	Acetone	C <sub>3</sub> H <sub>6</sub> O	0.799
10	2-Butanone	C <sub>4</sub> H <sub>8</sub> O	0.784
11	Cyclohexanone	C <sub>6</sub> H <sub>10</sub> O	0.697
12	Formaldehyde	CH <sub>2</sub> O	0.967
13	Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	0.824
14	Propanal	C <sub>3</sub> H <sub>6</sub> O	0.799
15	Benzaldehyde	C <sub>7</sub> H <sub>6</sub> O	0.532
16	Ethane	C <sub>2</sub> H <sub>6</sub>	0.891
17	Propane	C <sub>3</sub> H <sub>8</sub>	0.835
18	Butane	C <sub>4</sub> H <sub>10</sub>	0.804
19	Pentane	C <sub>5</sub> H <sub>12</sub>	0.786
20	Hexane	C <sub>6</sub> H <sub>14</sub>	0.773
21	Heptane	C <sub>7</sub> H <sub>16</sub>	0.763
22	Octane	C <sub>8</sub> H <sub>18</sub>	0.756
23	Nonane	C <sub>9</sub> H <sub>20</sub>	0.751
24	Decane	C <sub>10</sub> H <sub>22</sub>	0.747
25	Ethylene	C <sub>2</sub> H <sub>4</sub>	0.706
26	Propene	C <sub>3</sub> H <sub>6</sub>	0.706
27	1-Butene	C <sub>4</sub> H <sub>8</sub>	0.706
28	2-Butene, (Z)-	C <sub>4</sub> H <sub>8</sub>	0.706
29	2-Butene, (E)-	C <sub>4</sub> H <sub>8</sub>	0.706
30	1-Pentene	C <sub>5</sub> H <sub>10</sub>	0.706
31	2-Pentene, (E)-	C <sub>5</sub> H <sub>10</sub>	0.706
32	2-Pentene, (Z)-	C <sub>5</sub> H <sub>10</sub>	0.706
33	Benzene	C <sub>6</sub> H <sub>6</sub>	0.506
34	Naphthalene	C <sub>10</sub> H <sub>8</sub>	0.470
35	Anthracene	C <sub>14</sub> H <sub>10</sub>	0.455
36	Phenanthrene	C <sub>14</sub> H <sub>10</sub>	0.455
37	Pyrene	C <sub>16</sub> H <sub>10</sub>	0.440
38	Styrene	C <sub>8</sub> H <sub>8</sub>	0.506
39	$\alpha$ -Methylstyrene	C <sub>9</sub> H <sub>10</sub>	0.527
40	Toluene	C <sub>7</sub> H <sub>8</sub>	0.533
41	Benzene, 1,2-dimethyl-	C <sub>8</sub> H <sub>10</sub>	0.554
42	Benzene, 1,3-dimethyl-	C <sub>8</sub> H <sub>10</sub>	0.554
43	<i>p</i> -Xylene	C <sub>8</sub> H <sub>10</sub>	0.554
44	Ethylbenzene	C <sub>8</sub> H <sub>10</sub>	0.554
45	Benzene, 1,2,4-trimethyl-	C <sub>9</sub> H <sub>12</sub>	0.571

46	Benzene, 1,2,3-trimethyl-	C <sub>9</sub> H <sub>12</sub>	0.571
47	Benzene, 1,2,4,5-tetramethyl-	C <sub>10</sub> H <sub>14</sub>	0.584
48	Benzene, 1,2,3,5-tetramethyl-	C <sub>10</sub> H <sub>14</sub>	0.584
49	Benzene, 1,2,3,4-tetramethyl-	C <sub>10</sub> H <sub>14</sub>	0.584
50	Benzene, pentamethyl-	C <sub>11</sub> H <sub>16</sub>	0.595
51	Benzene, hexamethyl-	C <sub>12</sub> H <sub>18</sub>	0.604
52	Dimethyl ether	C <sub>2</sub> H <sub>6</sub> O	1.009
53	Ethoxy ethane	C <sub>4</sub> H <sub>10</sub> O	0.882
54	Propane, 2-ethoxy-2-methyl-	C <sub>6</sub> H <sub>14</sub> O	0.832
55	Phenol	C <sub>6</sub> H <sub>6</sub> O	0.565
56	Phenol, 4-methyl-	C <sub>7</sub> H <sub>8</sub> O	0.586
57	Phenol, 3-methyl-	C <sub>7</sub> H <sub>8</sub> O	0.586
58	Phenol, 2-methyl-	C <sub>7</sub> H <sub>8</sub> O	0.586
59	Phenol, 2,6-dimethyl-	C <sub>8</sub> H <sub>10</sub> O	0.602
60	Phenol, 2,4-dimethyl-	C <sub>8</sub> H <sub>10</sub> O	0.602
61	Phenol, 2,5-dimethyl-	C <sub>8</sub> H <sub>10</sub> O	0.602
62	Phenol, 2,3-dimethyl-	C <sub>8</sub> H <sub>10</sub> O	0.602
63	Phenol, 3,5-dimethyl-	C <sub>8</sub> H <sub>10</sub> O	0.602
64	Phenol, 3,4-dimethyl-	C <sub>8</sub> H <sub>10</sub> O	0.602
65	Formic acid	CH <sub>2</sub> O <sub>2</sub>	1.308
66	Acetic acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	0.967
67	1-Naphthalenol	C <sub>10</sub> H <sub>8</sub> O	0.509
68	2-Naphthalenol	C <sub>10</sub> H <sub>8</sub> O	0.509
69	Furan	C <sub>4</sub> H <sub>4</sub> O	0.583
70	9,10-Anthraquinone	C <sub>14</sub> H <sub>8</sub> O <sub>2</sub>	0.484
71	<i>p</i> -Benzoquinone	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>	0.539
72	1,4-Naphthalenedione	C <sub>10</sub> H <sub>6</sub> O <sub>2</sub>	0.503
73	Hydroquinone	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	0.598
74	Dibenzo- <i>p</i> -dioxin	C <sub>12</sub> H <sub>8</sub> O <sub>2</sub>	0.506
75	1,2-Benzenediol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	0.598
76	Resorcinol	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	0.598
77	1,3,5-Trioxane	C <sub>3</sub> H <sub>6</sub> O <sub>3</sub>	0.967
78	Cyclopropane	C <sub>3</sub> H <sub>6</sub>	0.706
79	Cyclopentane	C <sub>5</sub> H <sub>10</sub>	0.706
80	Cyclohexane	C <sub>6</sub> H <sub>12</sub>	0.706
81	Cyclopropene	C <sub>3</sub> H <sub>4</sub>	0.571
82	Cyclobutene	C <sub>4</sub> H <sub>6</sub>	0.604
83	Cyclopentene	C <sub>5</sub> H <sub>8</sub>	0.625
84	1,3-Cyclopentadiene	C <sub>5</sub> H <sub>6</sub>	0.544
85	Cyclohexane, methyl-	C <sub>7</sub> H <sub>14</sub>	0.706
86	Cyclopentane, ethyl-	C <sub>7</sub> H <sub>14</sub>	0.706
87	Cyclohexane, ethyl-	C <sub>8</sub> H <sub>16</sub>	0.706
88	Naphthalene, 2-methyl-	C <sub>11</sub> H <sub>10</sub>	0.489
89	Naphthalene, 1-methyl-	C <sub>11</sub> H <sub>10</sub>	0.489
90	Acenaphthylene	C <sub>12</sub> H <sub>8</sub>	0.447
91	Acenaphthene	C <sub>12</sub> H <sub>10</sub>	0.476
92	Fluorene	C <sub>13</sub> H <sub>10</sub>	0.464
93	Fluoranthene	C <sub>16</sub> H <sub>10</sub>	0.440
94	Benz[ <i>a</i> ]anthracene	C <sub>18</sub> H <sub>12</sub>	0.447
95	Chrysene	C <sub>18</sub> H <sub>12</sub>	0.447
96	Perylene	C <sub>20</sub> H <sub>12</sub>	0.436

97	Coronene	C <sub>24</sub> H <sub>12</sub>	0.420
98	Isobutane	C <sub>4</sub> H <sub>10</sub>	0.804
99	Butane, 2-methyl-	C <sub>5</sub> H <sub>12</sub>	0.786
100	Butane, 2,3-dimethyl-	C <sub>6</sub> H <sub>14</sub>	0.773
101	Pentane, 2-methyl-	C <sub>6</sub> H <sub>14</sub>	0.773
102	Butane, 2,2-dimethyl-	C <sub>6</sub> H <sub>14</sub>	0.773
103	Pentane, 3-methyl-	C <sub>6</sub> H <sub>14</sub>	0.773
104	1-Propene, 2-methyl-	C <sub>4</sub> H <sub>8</sub>	0.706
105	2-Butene, 2-methyl-	C <sub>5</sub> H <sub>10</sub>	0.706
106	1-Butene, 2-methyl-	C <sub>5</sub> H <sub>10</sub>	0.706
107	1-Butene, 3-methyl-	C <sub>5</sub> H <sub>10</sub>	0.706
108	Hexane, 2-methyl-	C <sub>7</sub> H <sub>16</sub>	0.763
109	Pentane, 2,4-dimethyl-	C <sub>7</sub> H <sub>16</sub>	0.763
110	Pentane, 2,2-dimethyl-	C <sub>7</sub> H <sub>16</sub>	0.763
111	Butane, 2,2,3-trimethyl-	C <sub>7</sub> H <sub>16</sub>	0.763
112	Pentane, 3-ethyl-	C <sub>7</sub> H <sub>16</sub>	0.763
113	Pentane, 2,2,4-trimethyl-	C <sub>8</sub> H <sub>18</sub>	0.756
114	Heptane, 2-methyl-	C <sub>8</sub> H <sub>18</sub>	0.756
115	Heptane, 3-methyl-	C <sub>8</sub> H <sub>18</sub>	0.756
116	Pentane, 2,3,4-trimethyl-	C <sub>8</sub> H <sub>18</sub>	0.756
117	Hexane, 2,3-dimethyl-	C <sub>8</sub> H <sub>18</sub>	0.756
118	Hexane, 3,4-dimethyl-	C <sub>8</sub> H <sub>18</sub>	0.756
119	Pentane, 3-ethyl-2-methyl-	C <sub>8</sub> H <sub>18</sub>	0.756
120	Hexane, 3-ethyl-	C <sub>8</sub> H <sub>18</sub>	0.756
121	Butane, 2,2,3,3-tetramethyl-	C <sub>8</sub> H <sub>18</sub>	0.756
122	Pentane, 3-ethyl-3-methyl-	C <sub>8</sub> H <sub>18</sub>	0.756
123	Pentane, 2,2,4,4-tetramethyl-	C <sub>9</sub> H <sub>20</sub>	0.751
124	Ethane, methoxy-	C <sub>3</sub> H <sub>8</sub> O	0.927
125	Ethoxy ethane	C <sub>4</sub> H <sub>10</sub> O	0.882
126	Propane, 2-ethoxy-2-methyl-	C <sub>6</sub> H <sub>14</sub> O	0.832
127	Ethyl acetate	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	0.824
128	Cyclopropanone	C <sub>3</sub> H <sub>4</sub> O	0.663
129	Cycloheptanone	C <sub>7</sub> H <sub>12</sub> O	0.701
130	Cyclobutanol	C <sub>4</sub> H <sub>8</sub> O	0.784
131	Cyclopentanol	C <sub>5</sub> H <sub>10</sub> O	0.773
132	Cyclohexanol	C <sub>6</sub> H <sub>12</sub> O	0.765
133	Propanal	C <sub>3</sub> H <sub>6</sub> O	0.799
134	Oxetane	C <sub>3</sub> H <sub>6</sub> O	0.799
135	Propylene oxide	C <sub>3</sub> H <sub>6</sub> O	0.799
136	2-Propen-1-ol	C <sub>3</sub> H <sub>6</sub> O	0.799
137	2-Furancarboxaldehyde	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>	0.572
138	Pentane, 3,3-dimethyl-	C <sub>7</sub> H <sub>16</sub>	0.763
139	Benzoic acid	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	0.564
140	Acetic acid, hydroxy-	C <sub>2</sub> H <sub>4</sub> O <sub>3</sub>	1.230
141	1,4-Dioxane	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	0.824

**Table 6.** H/C and O/C atomic ratios,  $H_{bo,0}$  and  $R_{\Delta H,bo}$  of the bio-oils from the pyrolysis with

$$T_{py} = 823 \text{ K.}$$

Biomass	Cedar	Pine	Willow	Bamboo	Sasa bamboo
H/C ratio, -	1.41	1.15	1.15	1.57	1.26
O/C ratio, -	0.32	0.26	0.20	0.45	0.36
$H_{bo,0,calc}$ , kJ mol-C <sup>-1</sup> (a)	-53	-34	-25	-80	-55
$R_{\Delta H,bo}$ , - (b)	0.675	0.614	0.603	0.728	0.653

(a) calculated by Eq.11. (b) calculated by Eq.16.

Remark: N and S contents in the chars were 0.1 - 0.4 wt%-daf and less than 0.1 wt%-daf, respectively.

**Table 7.** Optimized parameters for Eq.11.

Constant	Value
$a$	11.725
$b_1$	41.864
$b_2$	-57.075
$b_3$	17.739
$b_4$	-1.6393
$c_1$	-166.77
$c_2$	20.594
$c_3$	-64.368
$c_4$	25.368

**Table 8.** Error in estimating  $H_{bo,0}$  for the pyrolysis of biomass.

Biomass	Cedar	Pine	Willow	Bamboo	Sasa bamboo
Bio-oil yield, mol-C (mol-C-biomass) <sup>-1</sup>	0.43	0.39	0.43	0.41	0.44
Error in estimation of $H_{bo,0}$					
kJ (mol-C-bio-oil) <sup>-1</sup>	±10	±10	±10	±10	±10
kJ (mol-C-biomass) <sup>-1</sup>	±4.3	±3.9	±4.3	±4.1	±4.4
%-HHV-biomass	±0.91	±0.85	±0.94	±0.89	±0.99
MJ kg-biomass <sup>-1</sup>	±0.18	±0.17	±0.19	±0.17	±0.18

**Table 9.** Optimized parameters for Eq.16.

Constant or coefficient	Value
$d$	0.3576
$e_1$	0.09631
$e_2$	0.06586
$e_3$	-0.01440
$e_4$	0.0004993
$f_1$	0.4765
$f_2$	-0.8830
$f_3$	0.9358
$f_4$	-0.2691

**Table 10.** Error in estimating  $\Delta H_{bo}$  for the pyrolysis of biomass.

Biomass	Cedar	Pine	Willow	Bamboo	Sasa bamboo
Bio-oil yield, mol-C (mol-C-biomass) <sup>-1</sup>	0.43	0.39	0.43	0.41	0.44
Error in estimation of $\Delta H_{bo}$					
kJ (mol-C-bio-oil) <sup>-1</sup>	±1	±1	±1	±1	±1
kJ (mol-C-biomass) <sup>-1</sup>	±0.43	±0.39	±0.43	±0.41	±0.44
%-HHV-biomass	±0.09	±0.09	±0.09	±0.09	±0.10
MJ kg-biomass <sup>-1</sup>	±0.018	±0.017	±0.019	±0.017	±0.018

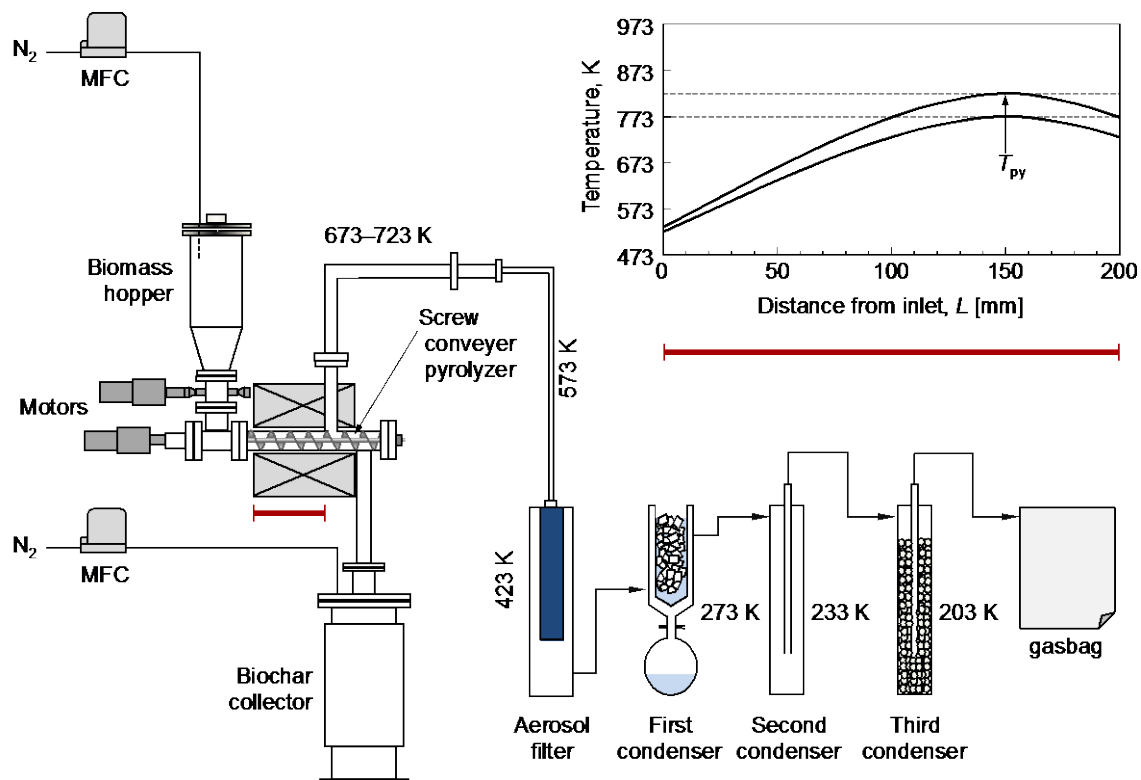
**Table 11.** Heat required for the pyrolysis ( $Q_{py}$ ) with  $T_{py} = 823$  K.

Unit	Cedar	Pine	Willow	Bamboo	Sasa bamboo
%-HHV-biomass	6.7	7.8	7.4	7.7	8.4
kJ (mol-C-bm) <sup>-1</sup>	31.4	35.9	33.5	35.4	37.6
MJ (kg-daf-biomass) <sup>-1</sup>	1.3	1.5	1.5	1.5	1.6

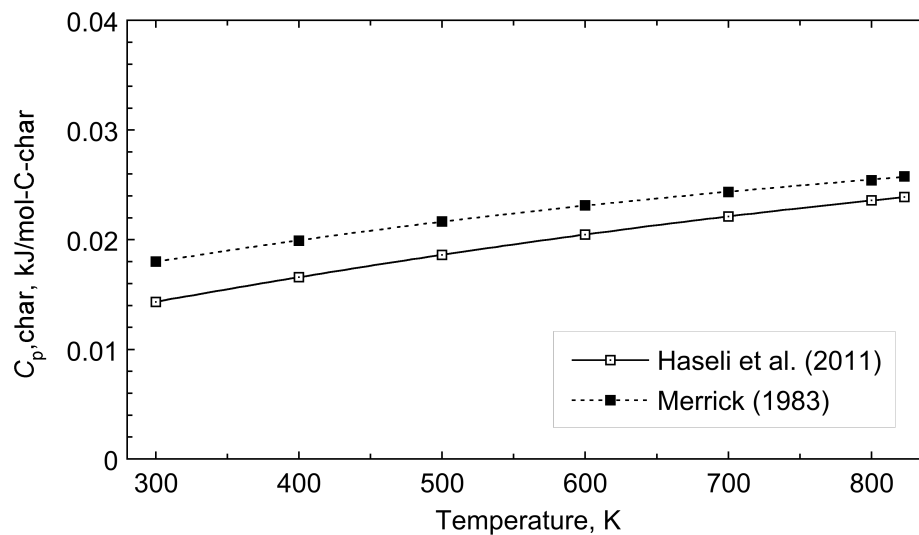
**Table 12.** Effects of heating rate on the product distribution and  $Q_{py}$  for the pyrolysis of cedar with  $T_{py} = 773$  K.

$T_{py}$	K	773	773	773	773
Heating rate <sup>(a)</sup>	K min <sup>-1</sup>	32	64	160	320
$Q_{py}$	%-HHV-dry-bm	5.5	5.7	5.8	6.0
	MJ kg-dry <sup>-1</sup>	1.1	1.1	1.2	1.2
Product yield					
H <sub>2</sub>	mol (100-mol-C-biomass) <sup>-1</sup>	0.48	0.53	0.35	0.75
H <sub>2</sub> O		28.5	26.8	23.9	23.7
CO	mol-C (100-mol-C-biomass) <sup>-1</sup>	8.0	8.7	7.8	8.2
CO <sub>2</sub>		6.1	5.6	5.5	4.9
CH <sub>4</sub>		2.6	2.5	2.2	2.1
C <sub>2</sub> H <sub>4</sub>		0.6	0.4	0.3	0.4
C <sub>2</sub> H <sub>6</sub>		0.6	0.2	0.2	0.2
C <sub>3</sub> H <sub>6</sub>		0.5	0.2	0.2	0.2
C <sub>3</sub> H <sub>8</sub>		0.2	0.1	0.0	0.0
C <sub>4</sub> H <sub>8</sub>		0.5	0.1	0.1	0.1
CH <sub>3</sub> OH		0.2	0.1	0.1	0.1
CH <sub>3</sub> CHO		0.1	0.0	0.0	0.0
Bio-oil		32.6	37.4	42.8	45.8
Char		47.9	44.7	40.8	38.0
H/C of bio-oil	(atomic ratio)	1.43	1.50	1.52	1.44
O/C of bio-oil		0.31	0.32	0.36	0.35

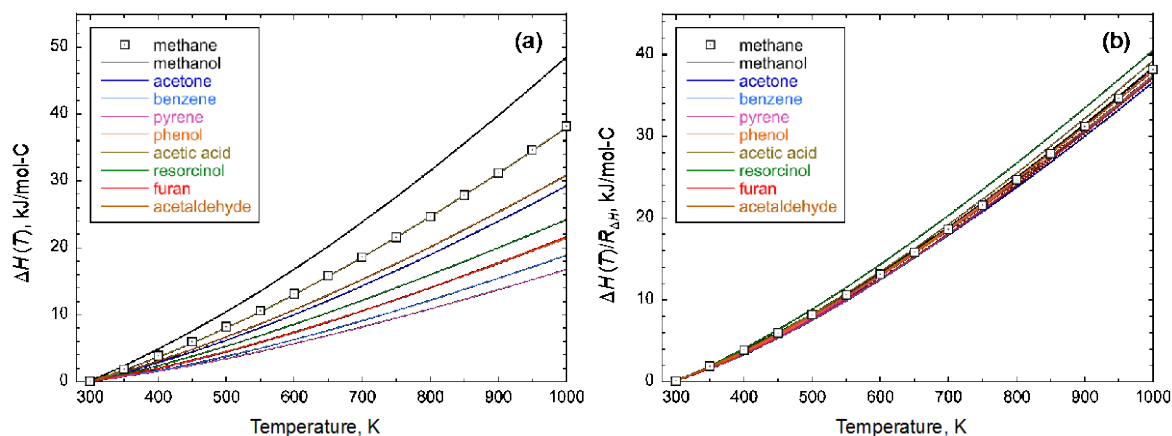
(a) Heating rate was calculated from the difference in temperature at reactor inlet (523 K) and  $T_{py}$  (= 773 K) and average residence time of cedar chips within the section between the reactor inlet and the position with  $T_{py}$ .



**Figure 1.** Schematic of apparatus for pyrolysis and temperature distribution in pyrolyzer.

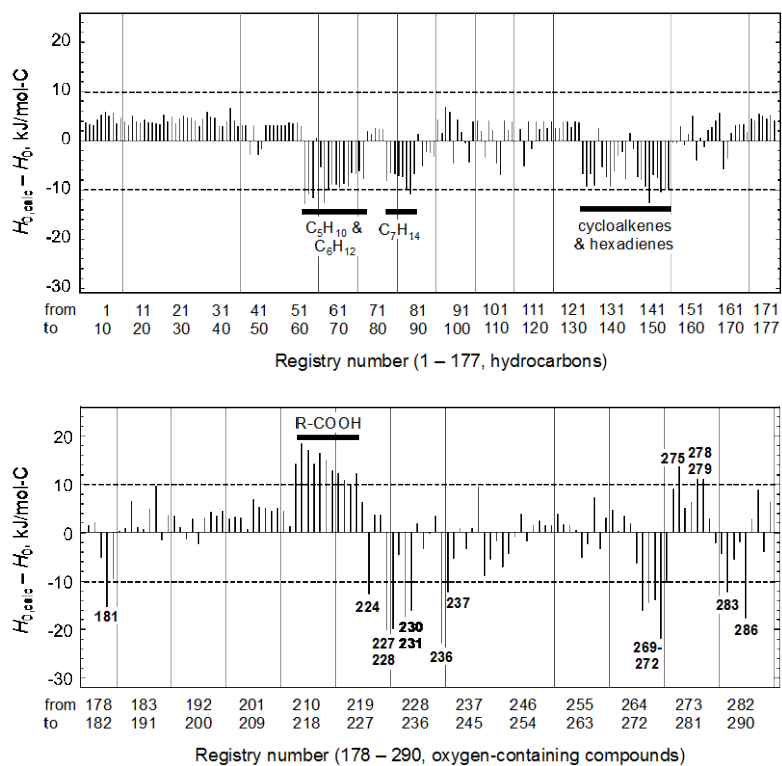


**Figure 2.** Specific heat of char reported previously.<sup>1,2</sup>

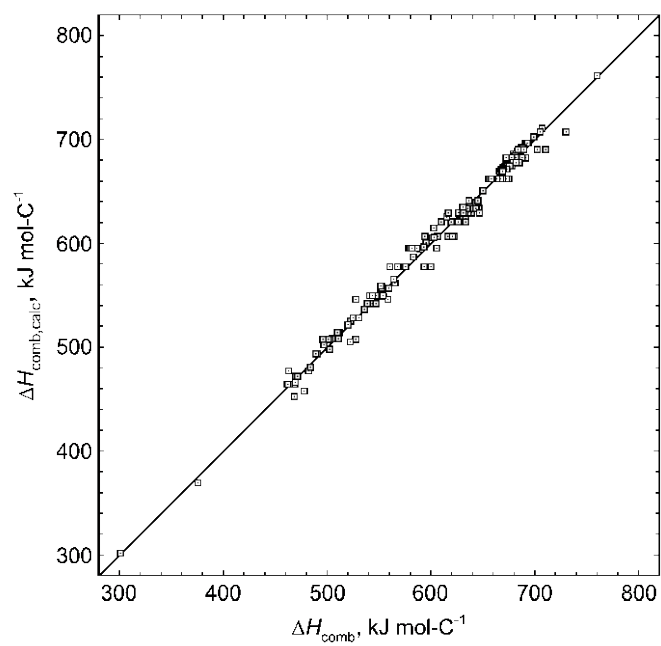


**Figure 3.** (a) Change of enthalpy ( $\Delta H$ ) for methane and other selected compounds as a function of temperature. (b) Estimation of  $\Delta H$  of methane ( $\Delta H_{\text{methane}}$ ) from  $\Delta H$  of another compound by Eq.14 with optimized set of parameters (see Table 5).

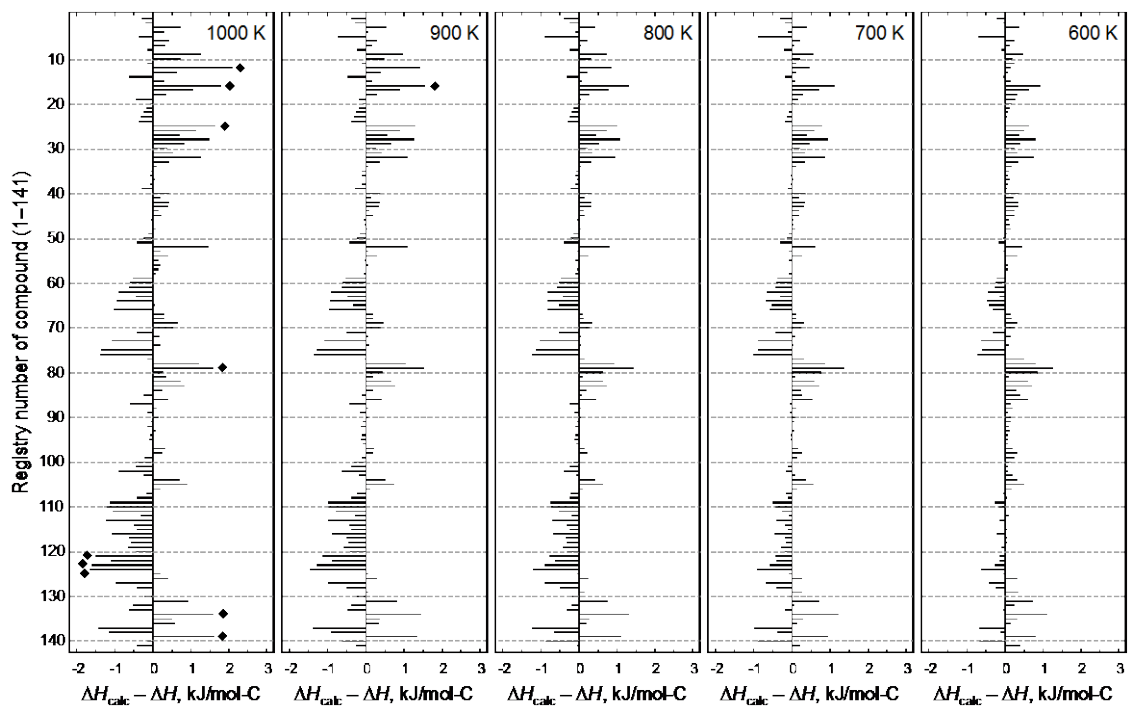




**Figure 4.** Difference between  $H_0$  calculated by Eq.11 and that available in literature for 290 organic compounds.



**Figure 5.** Relationship between  $\Delta H_{\text{comb,calc}}$  and  $\Delta H_{\text{comb}}$  for 290 compounds.



**Figure 6.** Error in estimation of  $\Delta H$  for 141 compounds listed in Table 4.

Keys:  $|\Delta H_{\text{calc}} - \Delta H| > 1.5 \text{ kJ mol}^{-1}$ .